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ABSTRACT

The molecular geometry of a series of trimethylene bridged ferrocene derivatives has been studied by means of Mössbauer effect. It was found that the planarity of the cyclopentadienyl rings of these ferrocene derivatives and, by inference, the ring-metal bond strength depend on the number and the position of the trimethylene bridges.

АННОТАЦИЯ

Молекулярная геометрия ряда производных ферроцена, содержащих триметиленовые мостики изучалась с помощью эффекта Мессбауэра. На основе полученных результатов показано, что планарность циклопентадиениловых кольцов в этих соединениях, и следовательно, также прочность π-связи между ними и атомом железа зависит от числа и позиции триметиленовых мостиков в молекуле.

KIVONAT

A ferrocén trimetilén-hidas származékainak sorozatát tanulmányoztuk Mössbauer-effektus segitségével. Az eredmények arra utalnak, hogy e ferrocén-származékok ciklopentadienil-gyürüinek planaritása és következésként a vas és a gyürük közötti π-kötések erőssége megváltozik, illetve csökken a trimetilénhidak számától és helyzetétől függően.

A new field of organometallic chemistry was opened with the discovery of bicyclopentadienyl iron(II) in 1951 and with the elucidation of its structure in 1952 /1,2/. Ferrocene and its many related compounds metallocenes differ from classical organometallic compounds in that instead of being σ--bounded to a specific carbon atom, the metal atom is bonded simultaneously to all ten of the carbon atoms via the d orbitals of the iron and the π orbitals of the rings (Fig.1). Similar sandwiches had been previously prepared between two benzene rings and chromium but the recognition of the structura awaited the discovery of ferrocene /3/. Many related compounds including open faced sandwiches are now know.

Considerable work has been odne on structural properties of this metallocene family of compounds. Among these were investigations of the effect of tilting the rings so that they are no longer parallel. Many metallocenes are normally of

this form, e.g. titanocene dichloride; others are forced to have non-planar rings by means of bridges across the rings that are too short to accommodate the required distance for parallel rings. Among the latter are the di- and trimethylene bridged derivatives of ferrocene and of the monomethylene bridged titanocene /4,5/.

The effects of ring tilting have been examined by means of various kinds of spectroscopy, especially by means of proton magnetic resonance and by Mössbauer spectroscopy /6,7/. An effect of ring tilting was found in the shifts of the ring protons in the proton magnetic spectrum but no significant effect was observed in the ^{57}Fe Mössbauer absorbtion spectrum. Since this paper deals with Mössbauer spectra, we shall concentrate only on these relevant results.

Mössbauer data for the ferrocene system were first reported in 1962 /8,9/. A large quadrupole splitting was observed in the Mössbauer spectrum of the ferrocene and the reduction of this quadrupole splitting to almost zero in the ferricinium-$/(C_5H_5)_2Fe/^+$-spectrum. The vanishing of quadrupole splitting can be explained by Ballhausens' molecular orbital model and by the results of Collins' magnetically perturbed Mössbauer experiment /10,11/. Concerning the Collins' determination, the sign of the electron field gradient (V_{ZZ}) is positive. The sign of the V_{ZZ} and the vanishing of the quadrupole splitting in the oxidation to the ferricinium ion is consistent with the predictions of the molecular orbital

model of Ballhausen. According to these explanations the major splitting is most likely caused by the 3d electrons, that is, the removal of one electron from the 3d molecular orbit causes the splitting to vanish. In the recent past a large variety of ring substituted ferrocenes have also been prepared and characterized by the Mössbauer method. It has turned out that the Mössbauer parameters of these substituted ferrocenes are fairly insensitive to the detailed structure of the molecule, with isomer shift being more insensitive than the quadrupole splitting /12,13/. The parameters for alkyl-substituted ferrocenes are the same, even when large bulky groups are involved (Table 1). In summary, all of the information on the ferrocenes published until now has indicated that the ring tilt and the relative positioning of the rings do not appreciably affect the metalring bonding. This is also in agreement with the theory of Ballhausen and Dahl / 10/. However, if a substituent causes electron delocalization from the metal, the contribution to the electric field gradient from the metal-d electrons is reduced with a consequent decrease in the quadrupole splitting /14/. This delocalization, however, has only a small effect on the isomer shift value.

Among the interannularly bridged ferrocene derivatives poly-bridged trimethylene-ferrocenes have also been prepared /15,16/. In these derivatives the cyclopentadienyl rings are linked by one or more bridges of three methylene groups.

Linking of the rings by one trimethylene ring apparently has no or a very small effect on the iron-ring bonding. Increasing the number of bridges could possibly introduce an effect because of some property other then ring tilting. The strain introduced by the trimethylene bridge may be relieved by several alternative means. The rings may be tilted, ring-ring distances may be shortered or the rings may become non-planar. The purpose of our investigation was to study the effect if any introduction of more than one bridge.

Experimental

With the exception of pentakistrimethyleneferrocene which is still not available, the bridged ferrocene derivatives were prepared by the methods developed by Rinehart et. al. /16/ with only minor modification. In the cases of the bridged ferrocenes the cyclopentadiene rings were linked by one or more trimethylene bridges (Fig.1). There are two possible isomers with two or three bridges. For example in the case of 12BTMF the cyclopentadiene rings were linked at adjacent positions, however, in the 13BTMF the bridges were nonadjacent.

The Mössbauer spectra of samples of all of these compounds were recorded by means of a constant acceleration type spectrometer using a ^{57}Co source in a chromium matrix. Metallic iron was used for the calibration. The measurements were carried out at room temperature. The Mössbauer parameters were evalua-

ted by a least squares fitting procedure. The isomer shift values refer to the centroid of the spectrum of metallic iron at room temperature.

Results and Discussion

The results of the measurements of the Mössbauer spectra in ferrocene and various bridged derivatives are summarized in Figures 2 and 3. They all have doublets due to quadrupole splitting. Except for TKTMF significant decrease in values of the quadrupole splittings (QS) and of the isomer shifts (IS) are observed as the number of bridges increases. Differences are observed between the isomers of both isomeric pairs, with larger decreases in QS and IS forthe isomers with nonadjacent bridges 13BTMF and 124TTMF . For the TKTMF the QS and IS are higher than the QS and IS of the three-bridged isomers and between the QS and IS of two-bridged isomers.

As mentioned earlier the bonding of the iron atom to the rings is not affected by alkyl substituents of cyclopentadiene rings. However, in the bridged alkyl derivatives it seems that the linkage of the cyclopentadiene rings by trimethylene bridges causes a significant electron delocalization increases for two and three bridges and decreases again for four. It should be noted that if only the values of QS and IS for ferrocene and TMF were available, it would be difficult to claim that there is a significant delocalization of electrons from the iron, and the conclusions of Good /12/ would

not be questioned.

Molecular models suggest that the preferred inter-ring separation of cc. 3.3 Å in ferrocene cannot be spanned by a chain of three C atoms unless the rings become mutually inclined /17,18/. In the trimethylene ferrocene the angle between ring planes is cc. 9° /7/. Ballhausen and Dahl have concluded that splaying of the rings about the metal atom can occur in principle without significant loss in metal-ring bond strength / 19/. However, linkage of the rings by two or more bridges could not only cause tilting of the rings but may also cause a the change in the planarity of rings. If the rings become non-planar the π-orbitals and consequently the metal--ring bond strength are expected to become weaker. The d orbital electron density on the iron would be lower and the QS and IS reduced. The nonadjacent bridges to the cyclopentadiene rings would be expected to cause larger perturbations in the planarity of the rings than would the adjacent bridges, and ultimately cause an even greater reduction in the QS and IS.

In the case of TKTMF it seems likely that theplanarity of the rings related to the three bridged derivatives is increased by linking of the fourth bridge due to the increased equivalence of the strain on all of the ring carbon atoms. In this case, the ring-ring distance would also be decreased and the ring-iron bond strengthened. The Mössbauer study of the five-bridged member in this series may provide further evidence on this hypothesis since symmetry considerations

demand planarity and a probable shortening of the ring-ring distance. Although this compound has apparently been prepared, it has not become available in sufficient quantity and purity for a Mössbauer measurement /20/.

The Mössbauer results reported here are explained by a hypothesis of the non-planarity of the rings. Additional studies necessary to confirm the hypothesis involve a direct structural determination by X-ray crystallography. Only the structure of 13BTMF has been reported in a preliminary fashion, and the structure of a keto derivative of TMF has been more thoroughly investigated /21/.

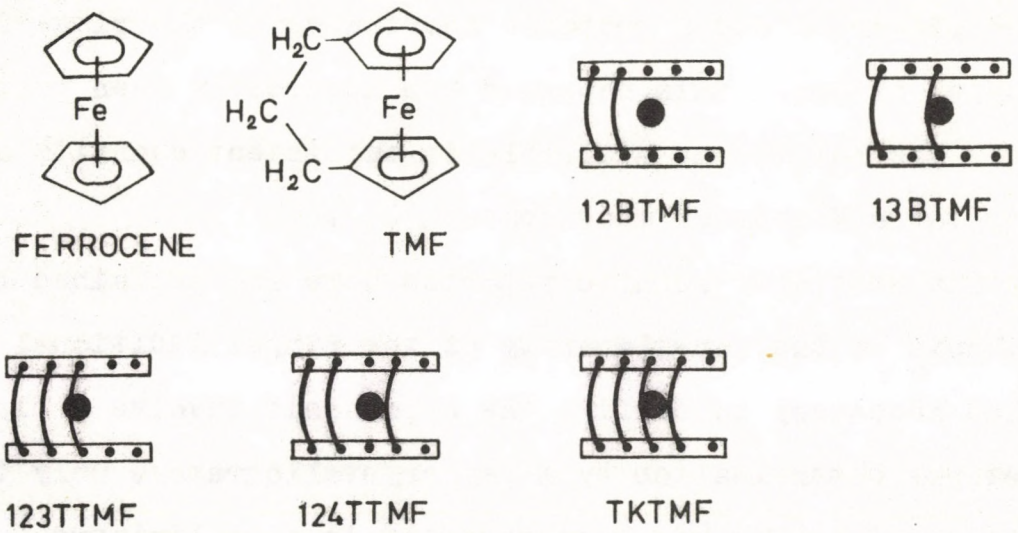

Figure 1

Ferrocene and its poly-bridged trimethylene derivatives. In each case the rectangles represent the cyclopentadienyl rings, the small solid circles the carbon atoms of the ring, the large solid circles the iron atoms and the arcs the carbon bridges.

TMF = 1,1'-trimethyleneferrocene;

12BTMF = 1,1',2,2'-bistrimethyleneferrocene;

13BTMF = 1,1',3,3'-bistrimethylene-ferrocene;

123TTMF = 1,1',2,2',3,3'-tristrimethyelenferrocene;

124TTMF = 1,1',2,2',4,4'-tristrimethyelenferrocene;

TKTMF = 1,1',2,2',3,3',4,4'-tetrakistrimethyleneferrocene

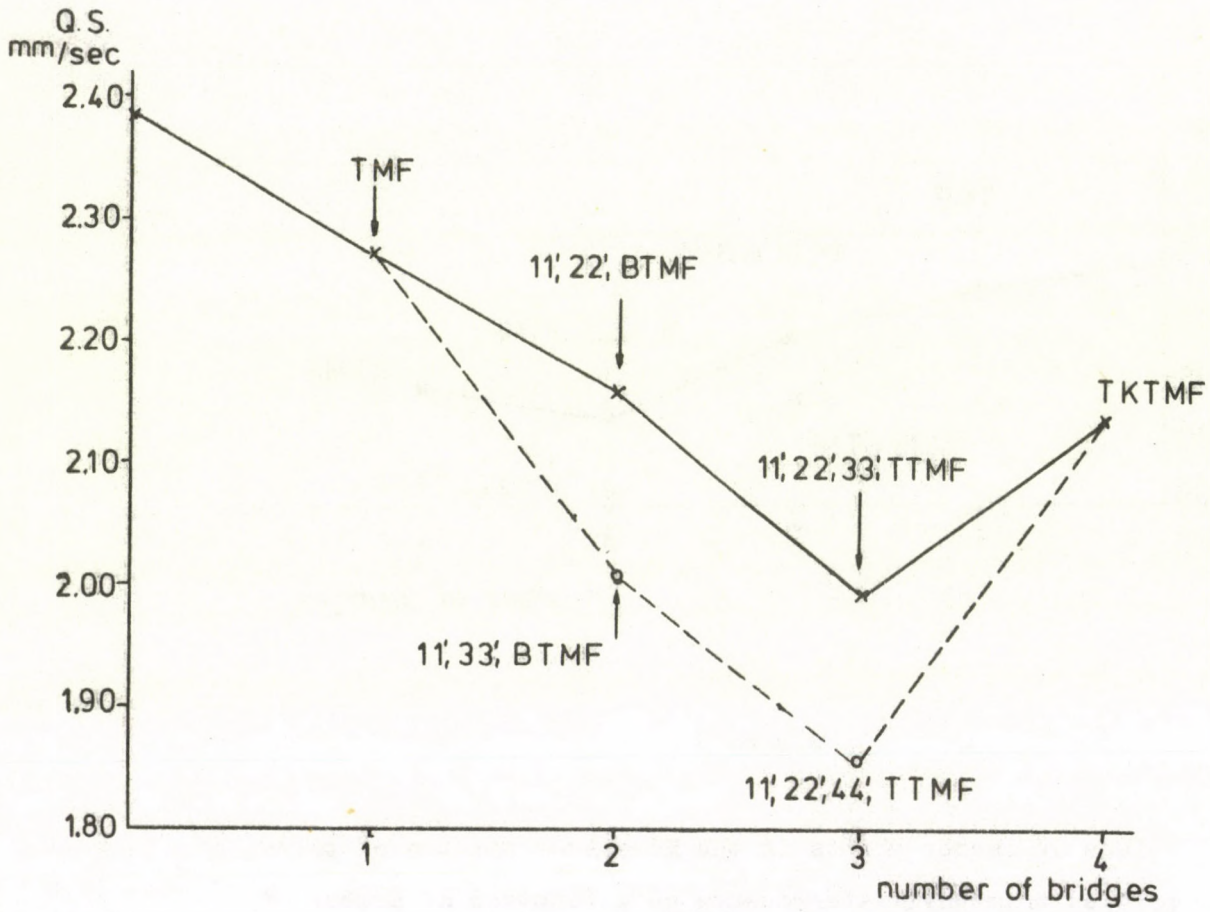

Figure 2

Values of quadrupole splittings in the Mössbauer spectra of ply-bridged trimethyleneferrocenes as a function of the number of the bridges. (Values of QS are $\pm$0.01 mm/s.)

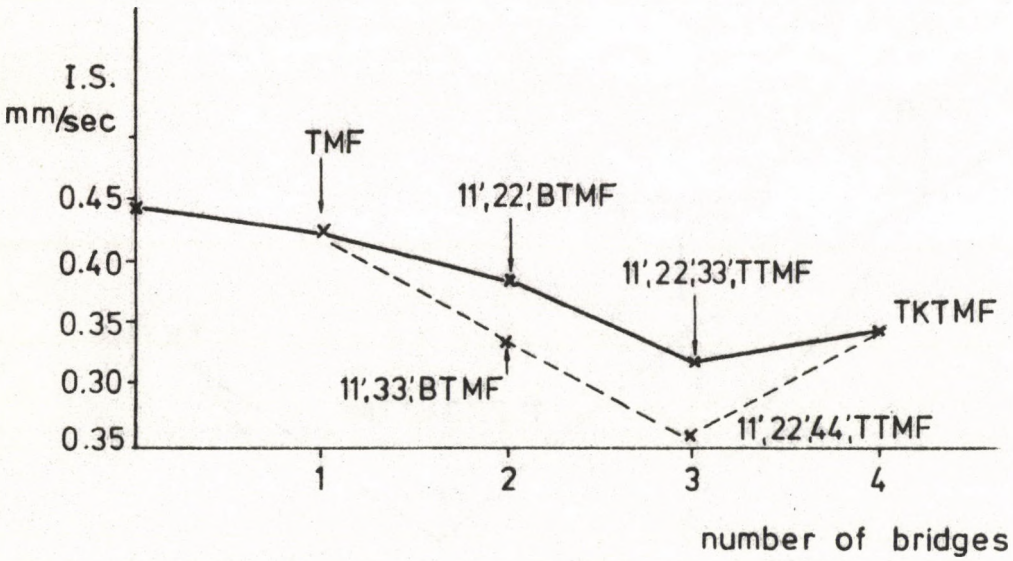

Figure 3

Values of isomer shifts in the Mössbauer spectra of poly-bridged trimethyleneferrocenes as a function of number of the bridges.(Values of IS are $\pm$0.01 mm/s.)

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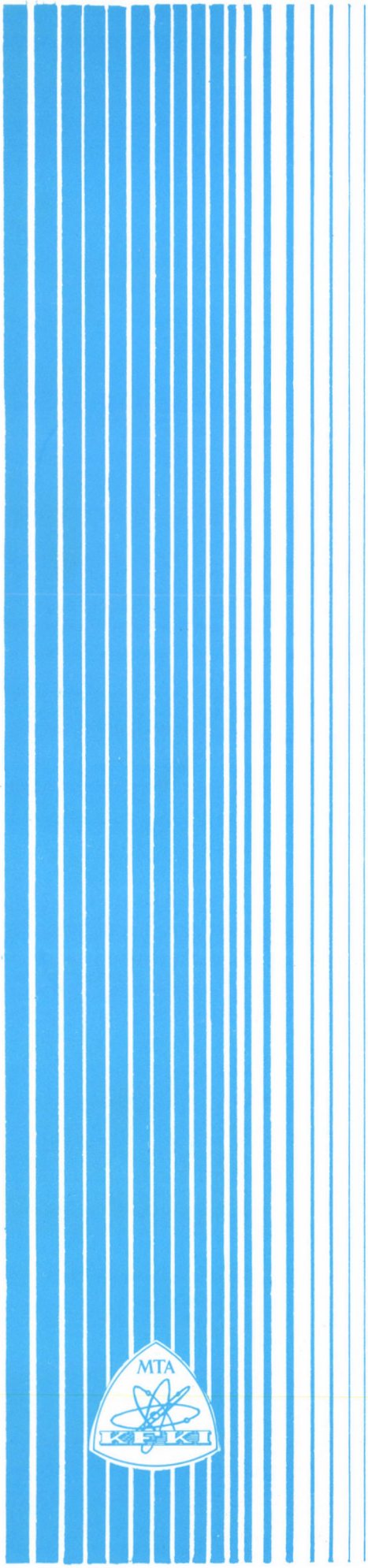
Table I

Mössbauer spectra and structural features of substituted ferrocenes [12]

Compound	Temp. K	IS mm/sec	QS mm/sec	Structural data
$(C_5H_5)_2Fe$	78	0.52	2.41	Rings are planar and parallel in staggered configuration ú
$(C_5H_5)Fe(C_5H_4CH_3)$	77	0.53	2.39	Ferrocene structure expected
$(C_5H_5)Fe[C_5H_4C(H)(OH)(C_6H_5)]$	78	0.51	2.41	- " -
$(C_5H_4Cl)_2Fe$	80	0.48	2.35	- " -
$(C_5H_5)Fe(C_5H_4Cl)$	80	0.50	2.42	- " -



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